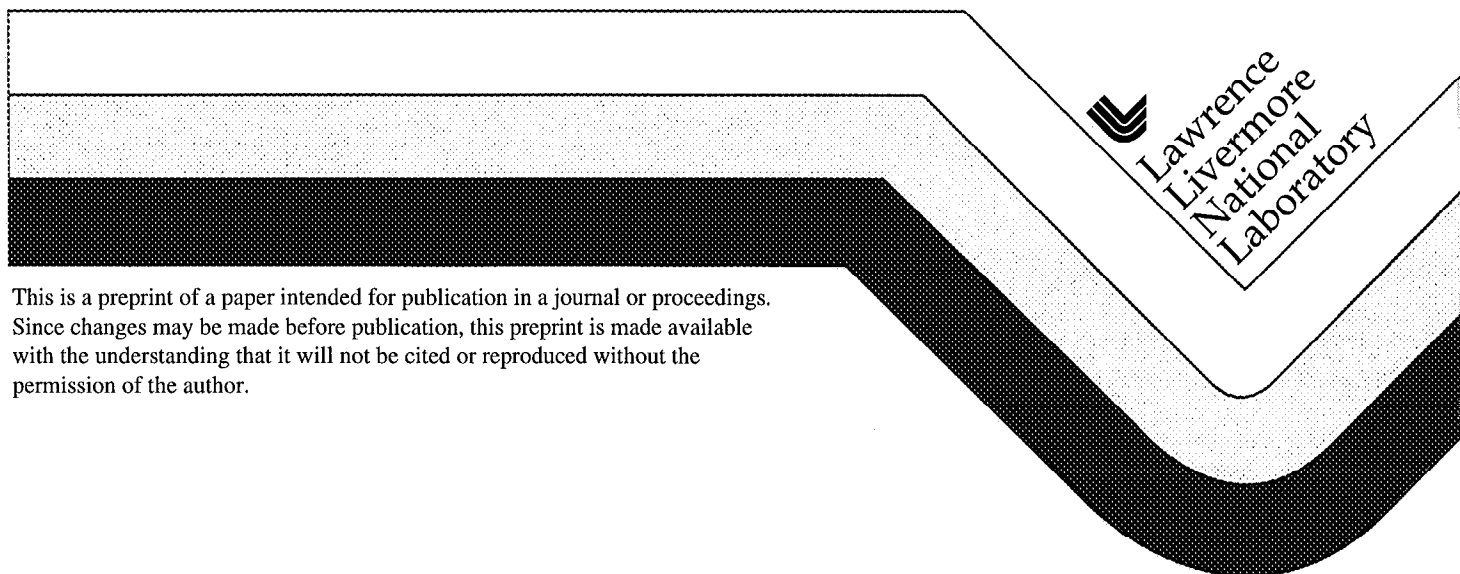# Thermodynamic and Structural Properties of Strongly Coupled Plasma Mixtures from the Perturbative HNC-Equation

H.S. Kang
F.H. Ree

DISCLAIMER

THERMODYNAMIC AND STRUCTURAL PROPERTIES OF STRONGLY COUPLED PLASMA MIXTURES FROM THE PERTURBATIVE HNC-EQUATION

Hong Seok Kang[1] and Francis H. Ree[2]

[1]Department of Chemistry and New Materials
Jeonju University, Chonju, KOREA
[2]University of California
Lawrence Livermore national Laboratory
Livermore, CA94551

INTRODUCTION

Recently, we developed the perturbative hypernetted-chain (PHNC) integral equation which can predict reliable thermodynamic and structural data for a system of particles interacting with either short range or long range (Coulomb) potential.[1,2] The present work extends this earlier work to mixtures. This is done by employing a reference potential which is designed to satisfy a thermodynamic consistency on the isothermal compressibility as described in the next section.

We test the present theory in Sec. III by applying it to plasma mixtures interacing with either an unscreened or a screened Coulomb potential. We made comparisons of results from the present theory with those from the best available theory, $i.e.$, Rosenfeld's density functional theory (DFT).[3] The DFT was shown to give internal energy with three to five figure accuracy compared to a wide range of Monte Carlo data.[4,5,6] Meanwhile, small deviations of excess internal energy from the so-called "liner mixing rule" (LMR)[7,8] are better predicted by a less sophiscated theory like the hypernetted-chain (HNC) equation. This rule relates thermodynamics of an unscreened mixture to those for individual components in a strongly coupled regime where the potential energy of a constituent particle is much larger than its kinetic energy.

We also apply the present thoery to a $H_2 + H$ mixture interacting with Morse potentials. For this sytem, comparison of thermodynamic properties and radial distribution functions from the present theory will be made with those from another successful theory of dense fluid, $i.e.$, the HMSA equation of Zerah and Hansen[9,10].

1

FORMULATIONS

The PHNC integral equation for a multi-component mixture employs a closure relation:

$$B_{ij}(r) = B_{ij,0}(r), \tag{1}$$

where $B_{ij}(r)$ and $B_{ij,0}(r)$ denote the bridge function for a system of interest and that for a reference system, respectively. The PHNC chooses the reference system so that the range (λ_{ij}) of the reference potential between species i and j depends on the temperature T and density ρ. For a one-component system $\lambda = \mathrm{Min}(a_{fcc}, r_{ij}^*)$ was shown to give a reliable result, where $a_{fcc}(= 2^{1/6}/\rho^{1/3})$ is the nearest neighbor distance at a given density for the face-centered cubic lattice and r_{ij}^* is the interatomic distance where the potential $V_{ij}(r)$ is the minimum.

For a mixture composed of $N_s(> 1)$ species, we need a more sophiscated choice. Namely, $\lambda_{ii}(i = 1, N_s)$ is chosen so that the partial isothermal compressibility $\partial(\beta P)/\partial \rho_i$ from the compressibility relation,

$$\frac{\partial(\beta P)}{\partial \rho_i} = 1 - \rho \sum_j x_j \int \mathrm{dr} \ c_{ij}(r), \tag{2}$$

gives the same result as that obtained from the virial equation,

$$\frac{\beta P}{\rho} = 1 - \frac{\beta \rho}{6} \sum_{i,j} x_i x_j \int \mathrm{dr} \ g_{ij}(r) r \frac{dV_{ij}(r)}{dr}. \tag{3}$$

Here $\beta = 1/kT$, where k is the Boltzmann constant; $c_{ij}(r)$ is the direct correlation function between species i and j, respectively. We choose λ_{ij} ($i \neq j$) to be additive, i.e., $\lambda_{ij} = (\lambda_{ii} + \lambda_{jj})/2$. For a plasma system, Eqs. (2) and (3) need to be modified to include contributions by the compensating background. This is done by replacing $c_{ij}(r)$ and $g_{ij}(r)$ by $c_{ij}(r) + \beta v_{ij}(r)$ and $g_{ij}(r) - 1$, respectively. Other details for choosing the reference potentials are similar to those described in Refs. 1 and 2. For example, it is assumed that the perturbation potentials are linear functions of r at $r \leq \lambda_{ij}$ and have continuous first derivatives at λ_{ij}.

Once the reference potentials are defined, $B_{ij,0}(r)$ is determined from the numerical solution of another set of coupled integral equations for the reference systems, using Ballone et al's closure relation[11]

$$B_{ij,0}(r) = [1 + s\gamma_{ij,0}(r)]^{1/s} - 1 - \gamma_{ij,0}(r), \tag{4}$$

with $s = 15/8$. Here $\gamma_{ij,0}(r) = h_{ij,0}(r) - c_{ij,0}(r)$, where $h_{ij,0}(r) = g_{ij,0}(r) - 1$ is the total correlation function between the species i and j. In summary, Eqs. (1) - (4) constitute a self-consistent cycle.

RESULTS AND DISCUSSION

Two-component plasma (TCP) corresponds to a simplest model of plasma mixture where ions with charge (in units of e) Z_1 and Z_2 move in a uniform background. Parameters describing this system are the coupling parameter $\Gamma = e^2/(kTa)$, Z_1, Z_2, and the mole fraction x of the species 2, where $a(= 3/4\pi\rho)^{1/3}$ is the ion-sphere radius. Instead of Γ, alternative description is possible in terms of $\Gamma_e = e^2/(kTa_e)$, where $a_e(= 3/4\pi\rho_e)^{1/3}$ is the electron radius and ρ_e is the electron density.

Table 1. Comparison of the excess internal energy for the TCP: the Monte Carlo data,[4, 5, 6] the PHNC (this work), and Rosenfeld's DFT.[3] Z_2 is the ionic charge of species 2 ($Z_1 = 1$); $\Gamma_e = (e^2/a_e kT)$, where a_e is the electron sphere radius; x is the mole fraction of species 2.

Z_2	Γ_e	x	βU^e Exact	PHNC	DFT
3	15	0.05	-15.79068 ± 0.00026	-15.78471	-15.7850
	15	0.1	-19.265 ± 0.001	-19.26000	-19.252
	15	0.2	-26.212 ± 0.001	-26.20914	-26.199
	15	0.5	-47.066 ± 0.002	-47.05487	-47.057
	20	0.01	-17.60188 ± 0.00026	-17.59037	-17.6033
	20	0.05	-21.31834 ± 0.00019	-21.31049	-21.3100
	20	0.1	-25.963 ± 0.001	-25.95929	-25.948
	20	0.2	-35.260 ± 0.002	-35.25469	-35.237
	20	0.5	-63.145 ± 0.002	-63.13663	-63.126
5	10	0.01	-9.20414 ± 0.00015	-9.20216	-9.20326
	10	0.05	-14.02753 ± 0.00015	-14.03313	-14.0081
	10	0.1	-20.05840 ± 0.00017	-20.06820	-20.0301
	10	0.2	-32.12399 ± 0.00023	-32.13566	-32.0974
	10	0.5	-68.33913 ± 0.00032	-68.34210	-68.3609
8	10	0.01	-10.75698 ± 0.00018	-10.76172	-10.7466

Table 1 compares the excess internal energy U^e for the TCP calculated from the PHNC, computer simulations,[4, 5, 6] and the DFT.[3] Note that $Z_1 = 1$ and $Z_2 > Z_1$. It shows that the PHNC is generally more accurate than the DFT, unless the species 2 is present at a very small mole fraction (= 0.01). And yet, more detailed calculation shows that the deviation from the LMR is not accurate enough. Figure 1 shows that the PHNC also gives accurate partial radial distribution functions, which is at least as accurate as the DFT. [See Fig. 5 of Ref. 3.]

Next, we briefly mention our results of the PHNC calculation on the Yukawa system, which is a more realistic model for the plasma than the one-component plasma (OCP) or the TCP. For a two-component Yukawa mixture composed of ions with charges Z_1 and Z_2, an interaction potential between the ions is represented by $V_{ij}(r) = Z_i Z_j e^2 e^{-\kappa r}/r$. In the linear screening approximation, the screening parameter κ is inversely proportional to the Debye length of background plasma. The potential energy of this system depends on five parameters, i.e., Γ, Z_1, Z_2, x, and κ. Although not shown here, excess internal energy of the one-component Yukawa system calculated from the PHNC is as accurate as those for the OCP in the entire range of $\kappa (< 1)$ investigated. This was confirmed by comparing the PHNC calculations with Monte Carlo data recently presented by Farouki and Hamaguchi.[12] In addition, we have found that λ which satisfies the self-consistency criterion is very close to a_{fcc} at a wide range of density around the freezing point. Typically, the difference between the two is within 5% of the latter for the Yukawa system. This is puzzling in that the weakly screened Yukawa system freezes to the body-centered cubic lattice.

Table 2 gives a comparison of the potential energy between Yukawa charges (U^{pp}) calculated from the PHNC and the HNC for the two-component Yukawa system. Also shown are those from the Yukawa mixing rule (YMR) [13] based on the calculations performed on the one-component Yukawa systems using the PHNC and the HNC. Here U^{pp} is related to the linear response energy $U_{lin.resp.}$ by
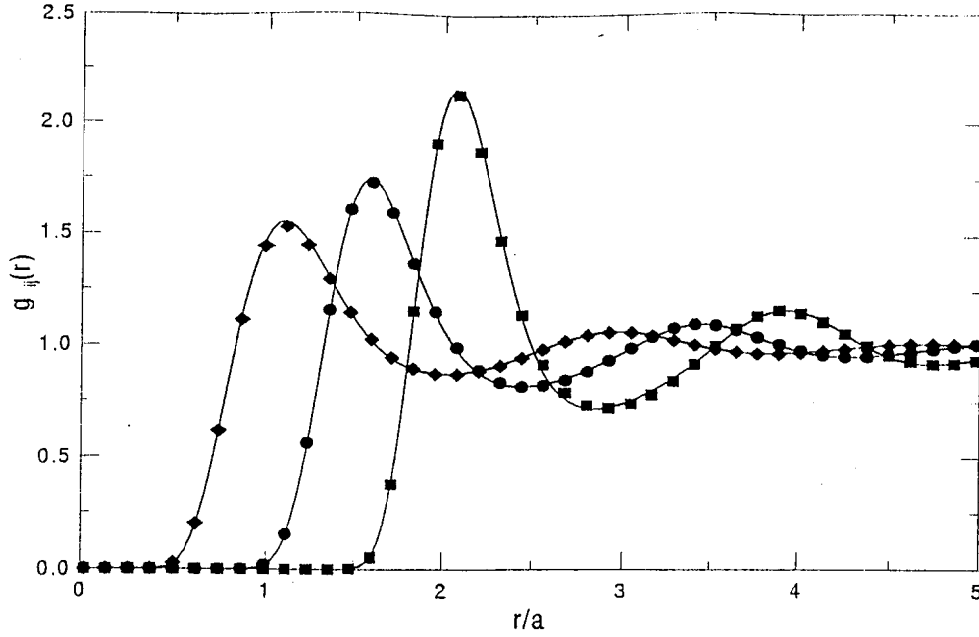
Figure 1. Radial distributions $g_{ij}(r)$ for an equimolar TCP mixture with $Z_1 = 1$ and $Z_2 = 5$ at $\Gamma_e = 10$. Diamonds, circles, and squares represent the Monte Carlo data of DeWitt, Slattery, and Chabrier[14] for the 11, 12, and 22 interactions, respectively. Solid lines correspond to the PHNC.

$$\beta U_{lin.resp.} = \beta U^{pp} - 3\Gamma \frac{<Z>^2}{2\kappa^2} - \frac{\Gamma}{2} <Z^2> \kappa \qquad (5)$$

$$= \frac{3\Gamma}{4\pi^2} \sum_{i,j} x_i x_j Z_i Z_j \int dk \ h_{ij}(k) \frac{k^2}{k^2 + \kappa^2}$$

$$-\frac{\Gamma}{2} <Z^2> \kappa, \qquad (6)$$

where distance is in units of the ion-sphere radius a. In terms of $u^{pp}(\equiv \beta U^{pp})$ the YMR can be expressed by

$$u^{pp}(Z_1, Z_2, \Gamma, x, \kappa) = (1 - x)u_1^{pp}(\Gamma_1, \kappa_1) + x u_2^{pp}(\Gamma_2, \kappa_2), \qquad (7)$$

where u_i^{pp} denotes the potential energy between Yukawa charges in the one-component system of the species i, and

$$\Gamma_i = (Z_i^2/R_i)\Gamma, \quad \kappa_i = \kappa R_i. \qquad (8)$$

Here R_i is obtained from the solution of the coupled algebraic equations

$$R_i^3 = \frac{Z_i Y(\kappa R_i)}{(1 - x)Z_1 Y(\kappa R_1) + x Z_2 Y(\kappa R_2)}, \quad (i = 1, 2) \qquad (9)$$

and

$$Y(t) = \frac{2t^3}{3[e^t(t - 1) + e^{-t}(t + 1)]}. \qquad (10)$$

Since the simulated data are not available, it is not possible to assess the accuracy of the PHNC. However, the table shows that the YMR holds very well for both of the PHNC and the HNC. We note that deviations of the HNC solution from the YMR are

4

Table 2. Potential energy between Yukawa charges U^{pp} calculated from the PHNC and the HNC at various values of the screening parameter κ at $\Gamma = 20$, $Z_1 = 1$, $Z_2 = 3$, and $x = 0.5$. Also shown are the results from the Yukawa mixing rule. PHNC-YMR denotes that the data are obtained from the rule based on the solutions of the PHNC for appropriate one-component systems. Similar definition applies to HNC-YMR.

κ	βU^{pp}			
	PHNC	PHNC-YMR	HNC	HNC-YMR
0.4	688.223	688.234	688.695	688.687
0.6	279.2484	279.2531	279.7071	279.6985
0.8	140.2371	140.2366	140.6827	140.6750
1.0	78.7460	78.7468	79.1764	79.1688

Table 3. Comparison of the compressibility factor $\beta P/\rho$ and the excess internal energy U^e of an eqimolar $H + H_2$ mixture: Exact data, the PHNC, and the HMSA.[10] The exact data with standard deviations inside parentheses are obtained in this work using 10^6 to $2 \cdot 10^6$ configurations, while values without standard deviations are taken from Ref. 10.

T(K)	$\rho(A^{-3})$	$\beta P/\rho$			βU^e		
		Exact	PHNC	HMSA	Exact	PHNC	HMSA
1,000	0.06	3.123	3.124	3.110	0.675	0.674	0.664
	0.2	16.996(6)	17.086	17.053	7.518(4)	7.540	7.538
5,000	1.0	35.31	35.32	35.37	24.07	24.09	24.17
10,000	0.2	3.212	3.212	3.214	1.309	1.308	1.307
	10	18.410(1)	18.429	18.443	12.536(2)	12.548	12.549

almost constant and positive (≈ 0.008) at all κ values considered in the table. It will be interesting to check this relation at a strong screening condition ($\kappa \gg 1$), where the HNC is generally considered to be inaccurate.

Table 3 shows that the PHNC can predict reliable results for a mixture interacting with potentials for $H + H_2$ mixtures. We note that it gives slightly better results than the HMSA equation of Zerah and Hansen. [The potential parameters used in this work are the same as those in Ref. 10.] This is further supported by the heights of the first peak in the H_2-H_2 radial distribution function. They are 1.798 ± 0.005, 1.802, 1.69, and 1.72, for the Monte Carlo data obtained in this work, the PHNC, and the one- and two-parameter HMSA, respectively. In the two-parameter calculation, the HMSA determines two parameters in their "switching functions" from conditions of thermodynamic consistency of two partial compressibilities similarly to the PHNC. [The switching functions are used to mix the soft mean spherical approximation (SMSA) at small r and the HNC closure at large r.] On the one hand, the one-parameter HMSA calculation employs a single switching function and determines its parameter from the consistency in the total compressibility calculated from the virial theorem and the compressibility equation.

Acknowledgments

REFERENCES

1.   H. S. Kang and F. H. Ree, J. Chem. Phys. **103**, 3629 (1995).
2.   H. S. Kang and F. H. Ree, J. Chem. Phys. **103**, 9377 (1995).
3.   Y. Rosenfeld, Phys. Rev. E **54**, 2827 (1996).
4.   S. Ogata, H. Iyetomi, S. Ichimaru, and H. M. Van Horn, Phys. Rev. E **48**, 1344 (1993).
5.   " Strongly Coupled Plasma Physics," edited by W. Kraeft and M. Schlanges, World Scientific, Singapore (1996).
6.   H. E. DeWitt, W. L. Slattery, and G. Chabrier, Physica B **228**, 21 (1996).
7.   J. P. Hansen, G. M. Torrie, and P. Vieillefosse, Phys. Rev. A **16**, 2153 (1977).
8.   B. Brami, J. P. Hansen, and F. Joly, Physica A **95**, 505 (1979).
9.   G. Zerah and J. P. Hansen, J. Chem. Phys. **84**, 2336 (1986); J.P. Hansen and G. Zerah, Phys. Lett. **108A**, 277 (1985). Physica A **95**, 505 (1979).
10. D. Levesque, J. J. Weis, and G. Chabrier, J. Chem. Phys. **94**, 3096 (1991).
11. P. Ballone, G. Pastore, G. Galli, and D. Gazzillo, Mol. Phys. **59**, 275 (1986).
12. R. T. Farouki and S. Hamaguchi, J. Chem. Phys. **101**, 9885 (1994).
13. Y. Rosenfeld, Phys. Rev. E **47**, 2676 (1993).
14. H. E. DeWitt (private communication).

6